

It is also known that the shades obtained with these oxidation bases can be varied by combining them with couplers or color modifiers, the latter being chosen in particular from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds.

The variety of molecules used in oxidation bases and couplers allows a rich palette of colors to be obtained.

The so-called "permanent" color obtained by means of these oxidation dyes should moreover satisfy a number of requirements. Thus, it should have no drawbacks from the toxicological point of view, it should make it possible to obtain shades of the desired intensity and it should exhibit good resistance toward external agents (light, adverse weather conditions, washing, permanent waving, perspiration, rubbing).

The dyes should also make it possible to cover gray hair, and thus should be the least selective possible, that is to say they should make it possible to obtain the smallest possible differences in color all along the same keratinous fiber, which may indeed be differently sensitized (i.e. damaged) between its tip and its root.

The oxidation dyeing of keratinous fibers is generally carried out in an alkaline medium, in the presence of hydrogen peroxide. However, the use of alkaline media in the presence of hydrogen peroxide has the disadvantage of causing substantial degradation of the fibers, as well as decoloring of the keratinous fibers which is not always desirable.

The oxidation dyeing of keratinous fibers can also be carried out with the aid of oxidizing systems different from hydrogen peroxide such as enzymatic

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systems. Thus, it has already been proposed in Patent
US 3,251,742, Patent Applications FR-A-2,112,549,
FR-A-2,694,018, EP-A-0,504,005, WO95/07988, WO95/33836,
WO95/33837, WO96/00290, WO97/19998 and WO97/19999 to
5 dye keratinous fibers with compositions comprising at
least [lacuna] oxidation dye, or at least one melanin
precursor, in combination with enzymes of the laccase
type, said compositions being brought into contact with
atmospheric oxygen. These dyeing formulations, although
10 used under conditions which do not cause degradation of
the keratinous fibers comparable to that caused by
dyeings carried out in the presence of hydrogen
peroxide, lead to colors which are still inadequate
both from the point of view of homogeneity of the color
15 distributed along the fiber (unison), from the point of
view of chromaticity (luminosity) and of the dyeing
power.

In point of fact, the Applicant Company has
now just discovered that it is possible to obtain novel
20 dyes, which are capable of resulting in powerful
colorings without causing significant degradation of
the keratinous fibers, which exhibit low selectivity
and which exhibit good resistance to various attacks to
which the fibers may be subjected, by combining 3-
25 methyl-4-aminophenol, as oxidation base, and at least
one enzyme of laccase type.

This discovery forms the basis of the present
invention.

5 medium appropriate for dyeing:

- at least one enzyme of laccase type.

15 which the hair may be subjected (washing, permanent deformation).

this ready-to-use dyeing composition.

25 approximately of this weight.

chosen in particular from laccases of plant origin,

5 invention can also be obtained by biotechnology.

10 Application FR-A-2,694,018.

20 *Prunus persica* and *Pistacia palaestina*.

25 *Rhizoctonia praticola* and *Rhus vernicifera* such as

described, for example, in Patent Applications FR-A-2,112,549 and EP-A-504005, the laccases described in Patent Applications WO95/07988, WO95/33836,

5 thermophila, Rhizoctonia solani, Pyricularia orizae, or
variants thereof. There may also be mentioned the
laccase(s) derived from Trametes versicolor, Fomes
fomentarius, Chaetomium thermophile, Neurospora crassa,
Coriolus versicol, Botrytis cinerea, Rigidoporus
10 lignosus, Phellinus noxius, Pleurotus ostreatus,
Aspergillus nidulans, Podospora anserina, Agaricus
bisporus, Ganoderma lucidum, Glomerella cingulata,
Lactarius piperatus, Russula delica, Heterobasidion
annosum, Thelephora terrestris, Cladosporium
15 cladosporioides, Cerrena unicolor, Coriolus hirsutus,
Ceriporiopsis subvermisporea, Coprinus cinereus,
Panaeolus papilionaceus, Panaeolus sphinctrinus,
Schizophyllum commune, Dichomitius squalens and
variants thereof.

20 The laccases of fungal origin optionally
obtained by biotechnology will be preferably chosen.

The enzymatic activity of the laccases used in accordance with the invention and which have syringaldazine among their substrates can be defined from the oxidation of syringaldazine under aerobic conditions. The Lacu unit corresponds to the quantity of enzyme catalyzing the conversion of 1 mmol of syringaldazine per minute at a pH of 5.5 and at a

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benzene, 2,4-diamino-1-(β -hydroxyethyloxy)benzene,
 2-amino-4-N-(β -hydroxyethyl)amino-1-methoxybenzene,
 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane,
 sesamol, α -naphthol, 6-hydroxyindole, 4-hydroxyindole,
 5 4-hydroxy-N-methylindole, 6-hydroxyindoline,
 2,6-dihydroxy-4-methylpyridine, 1-H-3-methylpyrazole-5-
 one, 1-phenyl-3-methylpyrazole-5-one, 2,6-dimethyl-
 pyrazolo[1,5-b]-1,2,4-triazole, 2,6-dimethyl[3,2-c]-
 1,2,4-triazole, 6-methylpyrazolo[1,5-a]benzimidazole,
 10 and their addition salts with an acid.

When they are present, the coupler(s)
 preferably represent from 0.0001 to 8% by weight
 approximately of the total weight of the dyeing
 composition, and still more preferably from 0.005 to 5%
 15 by weight approximately of this weight.

The dyeing composition in accordance with the
 invention can also contain, in addition to the 3-
 methyl-4-aminophenol and/or its addition salts with an
 acid, at least one additional oxidation base which can
 20 be chosen from oxidation bases conventionally used for
 oxidation dyeing. They can be chosen in particular from
 para-phenylenediamines, double bases, para-
 aminophenols, ortho-aminophenols and heterocyclic
 oxidation bases.

25 Among the para-phenylenediamines, there may
 be mentioned more particularly by way of example para-
 phenylenediamine, para-tolylenediamine, 2-chloro-para-
 phenylenediamine, 2,3-dimethyl-para-phenylenediamine,

Among the para-phenylenediamines mentioned hereinabove, there are most particularly preferred para-phenylenediamine, para-tolylenediamine, 2-isopropyl-para-phenylenediamine, 2- β -hydroxyethyl-para-phenylenediamine, 2- β -hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis(β -hydroxyethyl)-para-

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Among the bisphenylalkylenediamines, there
5 may be mentioned more particularly by way of example
N,N'-bis(β -hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-
diaminopropanol, N,N'-bis(β -hydroxyethyl)-N,N'-bis(4'-
aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)-
tetramethylenediamine, N,N'-bis(β -hydroxyethyl)-N,N'-
0 bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(4-
methylaminophenyl)tetramethylenediamine, N,N'-
bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylene-
diamine, 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane,
and their addition salts with an acid.

15 Among the para-aminophenols, there may be
mentioned more particularly by way of example para-
aminophenol, 4-amino-3-fluorophenol, 4-amino-3-
hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-
hydroxymethylphenol, 4-amino-2-methoxymethylphenol,
20 4-amino-2-aminomethylphenol, 4-amino-2-(β -
hydroxyethylaminomethyl)phenol, 4-amino-2-fluorophenol,
and their addition salts with an acid.

Among the ortho-aminophenols, there may be mentioned more particularly by way of example

25 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 5-acetamido-2-aminophenol, and their addition salts with an acid.

preferably between 6 and 9 approximately. It can be adjusted to the desired value by means of acidifying or basifying agents commonly used in dyeing keratinous fibers.

5 The ready-to-use dyeing composition in accordance with the invention may also contain various adjuvants conventionally used in compositions for dyeing hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures
10 thereof, polymers, antioxidants, enzymes different from the laccases used in accordance with the invention, such as for example peroxidases or oxidoreductases containing 2 electrons, penetrating agents, sequestering agents, perfumes, buffers, dispersing
15 agents, thickeners, film-forming agents, preservatives, opacifying agents or vitamins.

Of course, persons skilled in the art will be careful to choose this or these optional additional compounds such that the advantageous properties
20 intrinsically attached to the ready-to-use dyeing composition in accordance with the invention are not, or substantially not, impaired by the addition(s) envisaged.

The ready-to-use dyeing composition in
25 accordance with the invention can be provided in various forms, such as in the form of liquids, creams, gels, optionally pressurized, or in any other form appropriate for dyeing keratinous fibers, in particular

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human hair. In this case, the 3-methyl-4-aminophenol and, if appropriate, the additional oxidation dyes and the enzyme(s) of laccase type are present in the same ready-to-use composition, and consequently said

- 5 composition should be free of gaseous oxygen, so as to avoid any premature oxidation of the oxidation dye(s).

The subject of the invention is also a method of dyeing keratinous fibers, and in particular human keratinous fibers such as hair, using the ready-to-use
10 dyeing composition as defined above.

According to this method, at least one ready-to-use dyeing composition as defined above is applied to the fibers for a sufficient time to develop the desired color, after which they are rinsed, optionally
15 washed with shampoo, rinsed again and dried.

The time necessary for the development of the color on the keratinous fibers is generally between 3 and 60 minutes and still more precisely 5 and 40 minutes.

20 According to one particular embodiment of the invention, the method comprises a preliminary step consisting in storing in a separate form, on the one hand, a composition (A) comprising, in a medium appropriate for dyeing, 3-methyl-4-aminophenol and/or
25 at least one of its addition salts with an acid and, on the other hand, a composition (B) containing, in a medium appropriate for dyeing, at least one enzyme of laccase type, and then in mixing them at the time of

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Another subject of the invention is a multi-compartment device or dyeing (kit) or any other multi-compartment packaging system in which a first compartment contains the composition (A) as defined above and a second compartment contains a composition (B) as defined above. These devices may be equipped with a means which makes it possible to deliver the desired mixture to the hair, such as the devices described in Patent FR-2,586,913 in the name of the applicant.

DYEING EXAMPLE

-	3-Methyl-4-aminophenol	0.25 g
20	- 5-N-(β -Hydroxyethyl)amino-2-methylphenol	0.30 g
-	Laccase obtained from <i>Rhus vernicifera</i> containing 180 units/mg sold by the company ICN	1.8 g
-	(C ₈ -C ₁₀)Alkyl polyglucoside in aqueous 25 solution containing 60% of active substance (A.S.), sold under the name ORAMIX CG110® by the company SEPPIC	8.0 g
-	Ethanol	20 g

- pH agent q.s. pH 6.5
- Demineralized water q.s. for 100 g

The ready-to-use dyeing composition described above was applied to locks of natural gray hair which
5 is 90% white for 40 minutes at a temperature of 30°C.
The hair was then rinsed and then dried.

The hair was dyed in a coppery gold shade.

In the dyeing composition described above,
the *Rhus vernicifera* laccase at 180 units/mg, sold by
10 the company Sigma, can be replaced by 1.0 g of
Pyricularia orizae laccase at 100 units/mg sold by the
company ICN.

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